CLAIMS

1. A catalytic composition for the (co)polymerization of ethylene and other α-olefins, comprising the following two components in contact with each other, or the product of their reaction:

(i) a metallocene complex of a metal M of group 4 of the periodic table, including at least one η^5-cyclopentadienyl group and at least one unsaturated hydrocarbyl group R', bonded to the metal M;

(ii) an ionizing activator consisting of at least one organic or organometallic compound capable of reacting with said metallocene complex (i) so as to form a positive ionic charge thereon by the extraction of an anion of an unsaturated hydrocarbylic organic group and formation of a non-coordinating anion with a delocalized ionic charge;

characterized in that said unsaturated hydrocarbyl group R' has the following formula (I):

$$-(A_x D_y U_z) R^1 \qquad (I)$$

wherein:

- A represents any monomeric unit deriving from a vinylaromatic group polymerizable by means of anionic polymerization, having from 6 to 20 carbon atoms;

- D represents any monomeric unit deriving from a conjugated diolefin polymerizable by means of anionic polymerization, having from 4 to 20 carbon atoms;
- U represents any generic optional monomeric unit deriving from an unsaturated compound copolymerizable with any of the above conjugated diolefins D or vinylaromatic compounds A;
- R^I represents hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms;
- the index "x" can be zero or an integer;
- the index "y" is an integer higher than zero;
- the index "z" can be zero or an integer ranging from 1 to 20; and
- the sum (x+y) is equal to or higher than 2.

2. The catalytic composition according to claim 1, wherein said activating component (ii) is selected from the compounds belonging to one of the following four types:

I) oxygenated organometallic compounds of metals of groups 13 or 14 of the periodic table;

II) non-coordinating ionic organometallic compounds;

III) non-coordinating Lewis acids, and

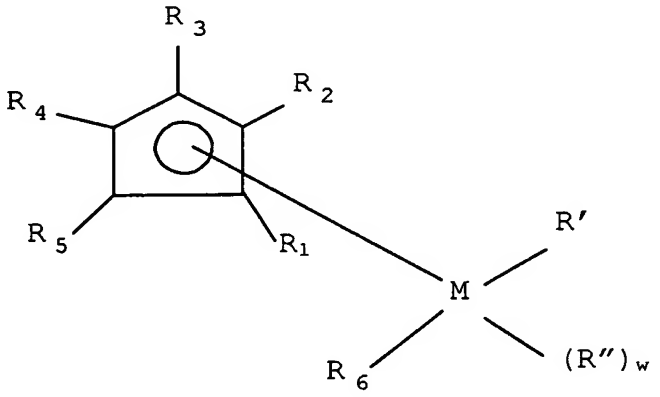
IV) polyfluorinated cyclopentadienyl compounds.

3. The catalytic composition according to any of the

claims 1 or 2, wherein said component (ii) is selected from the compounds of types II), III) and IV).

4. The catalytic composition according to any of the previous claims, wherein said (x+y) sum is between 2 and 50.

5. The catalytic composition according to any of the previous claims, wherein said metallocene complex in component (i) is represented by the following formula (II):



(II)

wherein:

- M is a metal selected from titanium, zirconium and hafnium, preferably from titanium and zirconium, coordinatively bonded to a first η^5-cyclopentadienyl group;
- R' is an unsaturated hydrocarbyl group as previously defined in claim 1;
- R" represents an optional organic or inorganic group bonded to the metal M, having an anionic nature, different from cyclopentadienyl or substituted cyclopen-

tadienyl;

- the groups R_1, R_2, R_3, R_4, R_5, each independently, represent an atom or a radical bonded to said first η^5-cyclopentadienyl group, selected from hydrogen or any other suitable organic or inorganic substituent of said cyclopentadienyl group;
- R_6 represents any other suitable organic or inorganic group of an anionic nature, bonded to the metal M;
- "w" has the value of 0 or 1, according to whether the group R" is present or absent in formula (II).

6. The catalytic composition according to any of the previous claims, wherein said metal M is selected from titanium and zirconium.

7. The catalytic composition according to any of the previous claims, wherein said metal M is zirconium in oxidation state +4.

8. The catalytic composition according to any of the previous claims, wherein said monomeric units of the D type in formula (I) derive from 1,3-diolefins with 4 to 20 carbon atoms.

9. The catalytic composition according to claim 8, wherein said 1,3-diolefin is selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene.

10. The catalytic composition according to any of the pre-

vious claims, wherein said monomeric units of the A type in formula (I) derive from hydrocarbyl vinyl aromatic compounds having from 8 to 15 carbon atoms.

11. The catalytic composition according to claim 10, wherein said vinyl aromatic compound is selected from styrene, α-methylstyrene, p-methylstyrene, vinylnaphthalene.

12. The catalytic composition according to any of the previous claims, wherein the sum of the indexes (x+y+z) in formula (I) is between 2 and 15.

13. The catalytic composition according to any of the previous claims, wherein "z" in formula (I) is equal to 0.

14. The catalytic composition according to any of the previous claims from 1 to 10, wherein "x" and "z" in formula (I) are both equal to 0 and said group R' consists of an oligomer of a conjugated diene D having an average polymerization degree from 2 to 15.

15. The catalytic composition according to any of the previous claims, wherein said group R^I in formula (I) represents an aliphatic, cycloaliphatic, aromatic or alkyl aromatic group having from 2 to 10 carbon atoms, preferably selected from tert-butyl, isopropyl, n-hexyl, cyclohexyl, benzyl, phenyl and toluyl.

16. The catalytic composition according to any of the pre-

vious claims from 5 to 15, wherein both groups R′ and R″, in the complex of formula (II), are independently oligomeric groups of formula (I), preferably having essentially the same formula.

17. The catalytic composition according to any of the previous claims from 5 to 16, wherein said group R_6, in the complex of formula (II), is "bridged" to said first cyclopentadienyl group, to form, as a whole, a cyclic structure including the metal M.

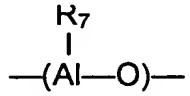
18. The catalytic composition according to any of the previous claims from 5 to 16, wherein said group R_6, in the complex of formula (II), represents a second cyclopentadienyl group η^5-coordinated to the metal M.

19. The catalytic composition according to claim 18, wherein said first and second cyclopentadienyl group are equal to each other.

20. The catalytic composition according to any of the previous claims from 5 to 16, wherein said complex of formula (II) includes three oligomeric groups of formula (I), in addition to said first η-cyclopentadienyl group.

21. The catalytic composition according to any of the previous claims, wherein said activator (ii) is an oligomeric or polymeric organo-oxygenated compound of aluminum.

22. The catalytic composition according to claim 21, wherein said activator (ii) is a polymeric aluminoxane including, in each molecule, from 4 to 70 repetition units having the following formula (VI):



(VI)

wherein R_7 is an alkyl C_1-C_6 group, preferably methyl.

23. The catalytic composition according to any of the previous claims from 2 to 20, wherein said activator (ii) is a compound of type II) consisting of an ionic organometallic compound of a metal M' selected from boron, aluminum or gallium, preferably boron.

24. The catalytic composition according to claim 23, wherein said activator (ii) is a compound or a mixture of compounds having one of the following general formulae:

$[(R_C)_xNH_{4-x}]^+ \cdot [B(R_D)_4]^-$; $[Ph_3C]^+ \cdot [B(R_D)_4]^-$;

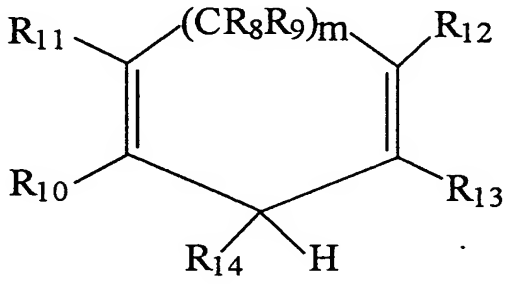
$[(R_C)_3PH]^+ \cdot [B(R_D)_4]^-$; $[Li]^+ \cdot [B(R_D)_4]^-$; $[Li]^+ \cdot [Al(R_D)_4]^-$;

wherein the subscript "x" is an integer between 0 and 3, each R_C group independently represents an alkyl or aryl radical with from 1 to 10 carbon atoms, and each R_D group independently represents a partially or, preferably, a totally fluorinated aryl radical having from 6 to 20 carbon atoms.

25. The catalytic composition according to any of the pre-

vious claims from 1 to 20, wherein said ionizing activator (ii) is a strong Lewis acid, preferably selected from triaryl boranes.

26. The catalytic composition according to any of the previous claims from 1 to 20, wherein said ionizing activator (ii) includes at least one fluorinated organic compound having the following formula (VII):



(VII)

wherein:

- each R_i (where "i" is an integer from 10 to 14), R_8 and R_9 group is a substituent of the di-unsaturated cycle independently selected from hydrogen, fluorine and an aliphatic or aromatic hydrocarbyl group, fluorinated or non-fluorinated, having from 1 to 20 carbon atoms, optionally bonded to a different hydrocarbyl R_i group adjacent thereto, to form a further condensed cycle with said di-unsaturated cycle,

  on the condition that at least three, preferably at least four, of the R_8, R_9, R_{10}, R_{11}, R_{12}, or R_{13}, groups, are independently selected, from the

group consisting of:

- fluorine, or
- a fluorinated alkyl group having the formula $-CF(R'_1R'_2)$, or
- a fluorinated aryl group Ar_F, substituted on the aromatic ring, with at least two groups selected from fluorine, a $-CF(R'_1R'_2)$ group as defined above, or a different Ar_F group, or
- a fluorinated vinyl group V_F, substituted on at least two positions of the double bond with groups selected from fluorine, a $-CF(R'_1R'_2)$ group or an Ar_F group, as defined above;

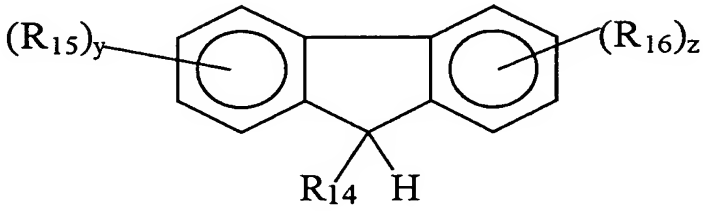
wherein each R'_1 or R'_2 can have any of the above meanings of the R_i groups, and at least one of them is fluorine or fluorinated alkyl at least in position 1, or a fluorinated aryl Ar_F as defined above, or a fluorinated vinyl group V_F as defined above; and

- "m" can have the value of 1 or 0.

27. The catalytic composition according to claim 26, wherein "m" in said fluorinated organic compound of formula (VII) is equal to 0.

28. The catalytic composition according to claims 26 or

27, wherein said compound of formula (VII) is a fluorinated fluorenyl compound having the following



(VIII)

formula (VIII):

wherein:

- R_{14} has the same meaning defined for the compounds of formula (VII);
- (y) is an integer from 1 to 4;
- (z) is an integer from 1 to 4;
- the groups R_{15} and R_{16} are, if necessary, independently substituents of each hydrogen atom of the respective aromatic ring in one or more of the four positions available, and are selected from fluorine or an aliphatic or aromatic hydrocarbyl group, fluorinated or non-fluorinated, having from 1 to 20 carbon atoms, optionally bonded to a different R_{15} or, R_{16} hydrocarbyl group, respectively, to form a further cycle,

on the condition that at least 3, preferably at least 4 of said R_4, R_{15} and R_{16} groups are independently selected from the group consisting of:

- fluorine, or

- a fluorinated alkyl group having the formula $-CF(R'_1R'_2)$, wherein each R'_1 or R'_2 group can have any of the above meanings of the R_i groups and at least one of these is fluorine, or fluorinated alkyl at least in position 1, or a fluorinated alkyl Ar_F as defined below, or a fluorinated vinyl group V_F as defined below, or
- a fluorinated aryl group Ar_F, substituted on the aromatic ring, with at least two groups selected from fluorine, a $-CF(R'_1R'_2)$ group as defined above, or a different Ar_F group, or
- a fluorinated vinyl group V_F, substituted on at least two positions of the double bond with groups selected from fluorine, a $-CF(R'_1R'_2)$ group or an Ar_F group, as defined above.

29. The catalytic composition according to any of the previous claims from 26 to 28, wherein said fluorinated organic compound having formula (VII) or (VIII) in said activator (ii), is added to the catalytic composition in a molar ratio between 1 and 10, with respect to the moles of the metallocene complex (i).

30. A process for the (co)polymerization of at least one α-olefin, characterized in that said α-olefin is (co)polymerized, under suitable polymerization conditions, in the presence of a catalytic composition com-

prising the following two components in contact with each other, or the product of their reaction:

(i) a metallocene complex of a metal M of group 4 of the periodic table, including at least one η^5-cyclopentadienyl group and at least one unsaturated hydrocarbyl group R', bonded to the metal M;

(ii) an ionizing activator consisting of at least one organic or organometallic compound capable of reacting with said metallocene complex (i) so as to form a positive ionic charge thereon by the extraction of an anion of an unsaturated hydrocarbylic organic group and formation of a non-coordinating anion with a delocalized ionic charge;

characterized in that said unsaturated hydrocarbyl group R' has the following formula (I):

$$-(A_x D_y U_z) R' \qquad (I)$$

wherein:

- A represents any monomeric unit deriving from a vinylaromatic group polymerizable by means of anionic polymerization, having from 6 to 20 carbon atoms;
- D represents any monomeric unit deriving from a conjugated diolefin polymerizable by means of anionic polymerization, having from 4 to 20 carbon at-

oms;

- U represents any generic optional monomeric unit deriving from an unsaturated compound co-polymerizable with any of the above conjugated diolefins D or vinylaromatic compounds A;
- R^I represents hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms,
- each index "x" and "y" can be independently zero or an integer, provided the sum (x+y) is equal to or higher than 2;
- the index "z" can be zero or an integer ranging from 1 to 20.

31. The process according to claim 30, wherein said catalytic composition is a composition according to one of the previous claims from 1 to 29.

32. The process according to either claims 30 and 31, wherein said α-olefin is (co)polymerized both in continuous and batchwise, in one or more steps, in suitable reactors, at low (0.1-1.0 MPa), medium (1.0-10 MPa) or high (10-150 MPa) pressure, at temperatures between 20 and 240 °C, optionally in the presence of an inert diluent.

33. The process according to any of the previous claims from 30 to 32, characterized in that it is carried out in solution or suspension, in a suitable inert medium

consisting of an aliphatic or cycloaliphatic hydrocarbon having from 3 to 15 carbon atoms, or a mixture thereof.

34. The process according to any of the claims from 30 to 32, wherein said α-olefin is polymerized in gas phase, at pressures ranging from 0.5 to 5 MPa and temperatures ranging from 50 to 150 °C, and said catalytic composition comprises at least one of the components (i) or (ii) on an inert solid carrier.

35. The process according to any of the claims from 30 to 34, for the (co)polymerization of ethylene.

36. The process according to claim 35, wherein ethylene is copolymerized with at least a second α-olefin having from 3 to 10 carbon atoms,

37. The process according to claim 36, wherein, in addition to said second α-olefin, a non-conjugated, aliphatic or alicyclic diene, having from 5 to 20 carbon atoms is copolymerized with ethylene.

38. The process according to any of the previous claims from 30 to 37, wherein said catalytic composition is prepared separately and subsequently put in contact with said at least one α-olefin.

39. The process according any of the previous claims from 30 to 37, wherein said catalytic composition is prepared by putting said components (i) and (ii) in con-

tact with each other, in the appropriate proportions, directly in the polymerization medium.

40. The process according to any of the previous claims from 30 to 38, for the production of linear high, medium and low density polyethylene.

41. A catalytic composition for the (co)polymerization of ethylene and other α-olefins, comprising the following two components in contact with each other, or the product of their reaction:

(i) a metallocene complex of a metal M of group 4 of the periodic table, including at least one η^5-cyclopentadienyl group and at least one unsaturated hydrocarbyl group R', bonded to the metal M;

(ii) an ionizing activator consisting of at least one organic or organometallic compound capable of reacting with said metallocene complex (i) so as to form a positive ionic charge thereon by the extraction of an anion of an unsaturated hydrocarbylic organic group and formation of a non-coordinating anion with a delocalized ionic charge, selected from the following classes of compounds:

I) non-coordinating ionic organometallic compounds;

II) non-coordinating Lewis acids, and

III) polyfluorinated cyclopentadienyl compounds.

characterized in that said unsaturated hydrocarbyl group R' has the following formula (I):

$$-(A_x D_y U_z) R^I \qquad (I)$$

wherein:

- A represents any monomeric unit deriving from a vinylaromatic group polymerizable by means of anionic polymerization, having from 6 to 20 carbon atoms;
- D represents any monomeric unit deriving from a conjugated diolefin polymerizable by means of anionic polymerization, having from 4 to 20 carbon atoms;
- U represents any generic optional monomeric unit deriving from an unsaturated compound copolymerizable with any of the above conjugated diolefins D or vinylaromatic compounds A;
- R^I represents hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms,
- each index "x" and "y" can be independently zero or an integer, provided the sum (x+y) is equal to or higher than 2;
- the index "z" can be zero or an integer ranging from 1 to 20.